Charge-Transfer Interaction between Phenothiazine- and Viologen Moieties Adsorbed to Quartz-Solution Interface as Studied by Optical Second Harmonic Generation (SHG)[1]

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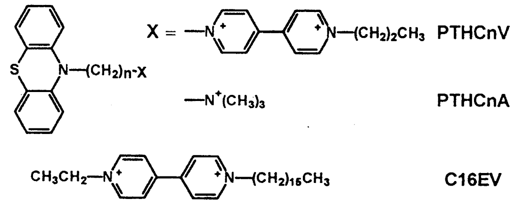
As to phenothiazine-viologen pair at quartz-solution interface, SHG was verified to serve as an excellent probe for charge-transfer interaction. The SHL intensity rapidly increased with the decrease of solvent polarity.

Surface SHG has frequently been used to study adsorption behavior of chemical species at solid-liquid interface.[2-4] Since SHG is enhanced in the presence of charge-transfer interactions, intensity of the second harmonic light (SHL) is expected to serve as a probe for charge-transfer (CT) interaction between the adsorbed species at interfaces. No precedent study of this type on solid-liquid interface has been reported. In the present study, SHG due to charge-transfer interaction at the interface was investigated by the use of the following phenothiazine-viologen linked compounds with strong charge-transfer properties[5]:



Amphiphilic compounds were prepared by the previously reported procedures.[5] Other chemicals in extra pure grades were used without further purification. Quartz substrate plates with negatively charged, hydrophilic surface were obtained by successive treatment of the plate (13 × 38 mm; 1.2 mm in thickness) in accordance with the procedures as described in a previous paper.[6] Water was completely removed from the surface as azeotropic mixture with benzene, and the plates were stored in spectro-grade n-hexane. The pretreated quartz plates were dipped into ethylacetate solutions of the amphiphilic compounds (50 μM) for more than 30 min. The treated plates were dried, and rinsed with purified ethylacetate to remove excessively adsorbed compounds on the surface.[7]

The SHG at plate surface was measured by the same setup and procedures as described in the previous paper.[6] Fundamental light (1064 nm) from a Nd:YAG laser (Continuum YG660B-10S, pulse duration 5-6 ns, repetition rate 2-10 Hz) was incident on the quartz plate. Intensity of second harmonic light (SHL) was measured with p-polarized lights at various incident angles (θ).

The quartz plate, as modified with an amphiphilic viologen (C16EV), was dipped into n-hexane solution of phenothiazine (50 μM) to measure SHG. A fringe pattern due to surface SHG was clearly observed with the sample as shown in Figure 1(a). No SHG was observed either with the viologen-modified plate alone (Figure 1(b)), or with the unmodified plate in the presence of phenothiazine (Figure 1 (c)). The SHL intensity was considerably reduced, when phenothiazine was replaced by carbazole with less electron-donating property. Thus, the observed SHG is strongly suggested as due to CT interaction between viologen at the modified surface and phenothiazine in the solution.

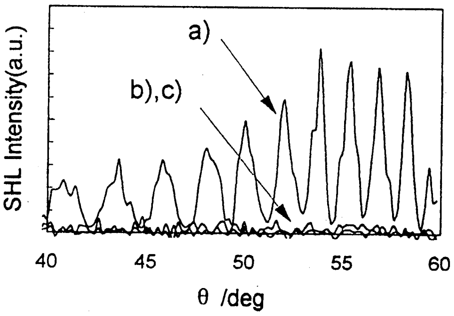


Figure 1. SHG as observed with amphiphilic viologen (C16EV)-modified substrate and phenothiazine in n-hexane: a) C16EV on quartz plate and phenothiazine in n-hexane (50 μM), b) the C16EV-modified plate alone in n-hexane, and c) the unmodified plate in n-hexane solution of phenothiazine (50 μM).

In order to assure 1:1 stoichiometric ratio between D and A moieties on the substrate surface, phenothiazine-viologen linked compounds were used to modify the quartz plate for the SHG measurement. The surface modification was carried out in exactly the same procedure as described above with C16EV. Amount of the linked compounds on the substrate surface was monitored by the absorption maximum at 260 nm due to phenothiazine moiety. After rinsing with ethylacetate, the substrate surface was rather sparsely covered by a monomolecular layer of linked compounds as judged from the absorbance.[8]

A remarkable SHG signal pattern due to PTHC8V was clearly observed with this sample as shown in Figure 2. The signal intensity was confirmed to show quadratic increase with laser power. Effects of spacer chain length on the SHL intensity were examined with three linked compounds (PTHCnV; n = 8,10, and 12). As to the linked compounds with longer spacers (n=10 and 12), the SHL intensity was reduced by ca 20% as compared with that for n=8 under the same conditions. Further reduction of SHL intensity was observed with a carbazole-viologen homologue (n=8).

The terminal viologen group was replaced by a trimethyl ammonium group to obtain a reference compound (PTHC12A). The absorption due to phenothiazine moiety again suggested that the substrate surface was rather sparsely covered by a monomolecular layer of the reference compound.[8] The reference compound on this modified quartz plate afforded negligibly small SHG as compared with that of the viologen homologue (Figure 2).

On the basis of above observations, one can conclude that neither viologen (Figure 1(b)) nor phenothiazine moiety (Figure 2, solid line), as an isolated chromophore, interacts with the

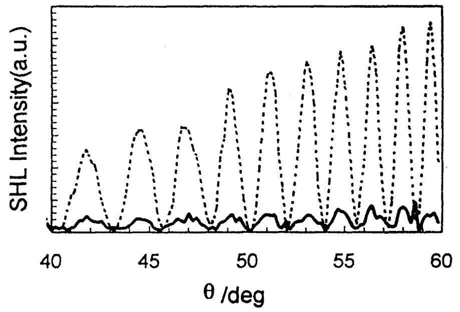


Figure 2. SHG due to a phenothiazine-viologen linked compound (PTHC8V) on the quartz plate (dotted line), and the reference (PTHC12A) with an ammonium group (solid line).

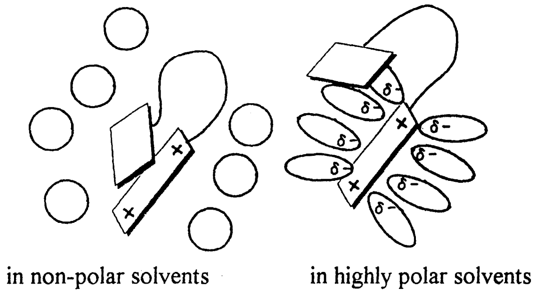
Table 1. Effects of solvent polarity on SHL intensity due to PTHC8V on quartz substrates

Solvent	Dielectric Constant	SHL Intensity (a.u.)
n-Hexane	1.9	290
Di(n-butyl)ether	3.1	180
Diethyl ether	4.3	110
Ethyl acetate	6.2	80

substrate surface to afford appreciable SHL intensity. The intensified SHL may be most reasonably explained as due to interaction between the phenothiazine and viologen moieties in the linked compounds at the substrate surface. In fact, the present authors previously reported observation of CT absorption at 550 nm with the linked compound (PTHC12V) in aqueous solutions.[5] The observed SHG enhancement is thus likely associated with the CT interaction between the donor- and acceptor moieties. An attempt was made to detect the CT absorption with the modified quartz plate. The absorption, however, was too small to be observed. Then, effects of solvent polarity on the SHL intensity were examined.

The SHG from PTHC8V-modified quartz plate was measured in four solvents with different dielectric constants: n-hexane, di(n-butyl) ether, diethyl ether, and ethyl acetate. A single PTHC8V-modified quartz plate was used to measure the SHG in the four solvents. The SHG measurements were repeated with the four solvents in different order to confirm the experimental reproducibility and stability of the modified surface. Each experiment with the specified solvent was followed by SHG measurement with the same modified quartz plate in n-hexane. Since the SHL intensity in n-hexane could be reproduced each time, the amount of phenothiazine moiety on the substrate was concluded to be the same throughout the experiment. Relative intensities of SHL in the four solvents at the peak top around 48 incident angles are compared in Table 1. The intensity clearly decreased with increase of the solvent polarity. The reason may be ascribed to increased solvation of the viologen moiety in more polar solvents, which will hinder direct contact between phenothiazine- and viologen moieties as illustrated in the following scheme:

Scheme 1.



For the simplicity, intramolecular CT interaction was assumed in illustrating the solvent effects. Contribution of intermolecular interaction can not be completely disregarded. Further studies are under progress to evaluate these two competing processes and other thermodynamic parameters relevant to SHG in this novel system.

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References and Notes

1 Contribution No.1020 from the Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University

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7 The rinsing solution was finally sonicated, and the effects were monitored by difference spectra due to phenothiazine moiety on the substrate. The results indicated that simple rinsing was good enough to remove the excessively adsorbed amphiphilic compounds in ethylacetate.

8 The absorbance at 260 nm for separately modified quartz plates was fairly reproducible (0.01 ± 0.002). Number of phenothiazine units on the modified surface was estimated on the basis of the absorbance and molar absorptivity of the amphiphilic compounds (8×10^4 $M^{-1}cm^{-1}$) in methanol solutions. The viologen derivative, for example, was thus suggested to cover 270 $Å^2$ per molecule in average. The value is several-fold larger than cross sections of viologen moiety as suggested by space-filling molecular models: 114 $Å^2$ for lying flat model, and 54.4 $Å^2$ for standing side on model. Thus, rather sparse coverage of the quartz surface by the viologen derivatives was suggested. Essentially the same result was obtained with the reference compound.